High performance tyre with tread band having an anisotropic underlayer stable upon temperature variation

The present invention relates to high performance tyres such as, for example, tyres designed for high-powered cars or, more generally, tyres intended

for applications involving high operating speeds.

Description of the Kelated Art

These tyres, which are commonly referred to as "HP" and "UHP" (High Performance and Ultra High Performance) tyres, are in particular those belonging to the Classes "V" and "Z" that respectively provide for maximum speeds over 210 Km/h and 240 Km/h, for which the operating performance is undoubtedly one of the most important features.

This performance depends both on the friction coefficient (or grip) and on the response to lateral stresses of the tyre during rolling on the road surface.

Usually the friction coefficient depends on the properties of the compound used for the tread, while the response to lateral stresses and to centrifugal forces depends on the tyre structure; for these reasons there exist structures designed to compensate for the force systems to which HP and UHP tyres are subject.

One of these structures envisages the presence of a so-called "0" layer, namely a layer of rubber reinforced by a cord which is usually heat-shrinkable, for example made of nylon, wound spirally in the circumferential direction around the tyre belt.

The winding angle of the cord with respect to a median (or equatorial) plane of the tyre is fairly small and it is for this reason that the layer in which it is located, is referred to as a "0" layer; the tread band is then mounted on top of this layer.

From Canadian patent CA 1228282 in the name of Bridgestone and European patent EP 592218 in the name of Sumitomo it is also known to form the tread band with what is commonly known as "cap and base" structure, namely consisting of two layers circumferentially arranged one upon the other wherein the radially innermost layer forms the "base" or underlayer, while the other outermost forms the "cap" and is the layer which is intended to roll on the road.

In particular, the first of these documents suggests to combine an underlayer with an external cap having a high grip and a predefined ratio between its modulus of elasticity and that of the underlayer, in order to improve the steering performance of the tyre at high speeds.

European patent EP 592218 teaches, on the other hand, to add reinforcing fibres to the compound of the underlayer and orienting them in a particular manner so as to obtain an anisotropic behaviour thereof with a different modulus of elasticity, respectively, in a circumferential and a transverse direction with respect to the tyre.

In this way it is possible to obtain a tyre with excellent stability during bends, a high level of comfort during travel as well as a low rolling resistance.

Finally, from European Patent Application EP 691218 published in 1996 it is known to manufacture tyres with properties which are substantially equivalent to those of tyres with a reinforcing layer consisting of nylon cords arranged at 0°, by providing, in place of the latter, a tread underlayer reinforced by fibres of a particular size and strength.

These fibres consist of materials such as polyamides (in particular aromatic polyamides shortly referred to as "aramides"), polyesters or polyolefins, which are already known in the art for their use in the manufacture of tyres.

For example, with regard to aramide fibres, a detailed description of their use in the tyre sector is given in the American patent US 4871004, which is hereby incorporated by reference.

One of the reasons justifying the use of the abovementioned fibres lies in the fact that they generally allow to achieve a good structural resistance with a reduced weight.

There are, however, certain technical aspects which must be taken into account when using the fibres in question.

Indeed, their use instead of, or in combination with, materials of the traditional type used in the manufacture of tyres, is an area which today is still not fully known: it is therefore important to be able to optimize the use of the fibres in

order to obtain the required features of the tyres.

The HP and UHP tyres currently known are not fully satisfactory from the point of view of their performance at high speed and over long operating periods: the present invention proposes to solve this problem by providing a high performance tyre having structural and operating features that remain substantially unvaried during the different conditions of use

unvaried during the different conditions of use.

Sommary of the Invention

The invention arises from the Applicant's realization that the characteristics of a high modulus and/or hardness of the compound of the underlayer, as an alternative to or in combination with each other, must also be guaranteed at the high speeds referred to above and in particular must not deteriorate with an increase in the temperature due to prolonged use at high speed, and that this object may be attained using the abovementioned fibres.

In particular the Applicant has discovered that the problem may be solved using a tyre wherein on the reinforcing layer with cord at 0°, there is applied a tread band with a "cap and base" structure whose underlayer has hardness and/or elasticity values which are substantially stable between 23°C and 100°C.

Owing to these features, in fact, the tyre ensures a uniform performance also at the high operating speeds which may cause a substantial increase in the temperature of the tread.

In accordance with one of its more specific aspects, the invention relates to a tyre wherein the hardness of the tread underlayer between 23°C e 100°C does not vary by more than five units on the IRHD (International Rubber Hardness Degrees) scale; preferably this variation must not exceed three units and, even better, one IRHD unit.

According to another more specific aspect of the invention, the tyre tread band has an underlayer with a dynamic modulus (E') which between 70°C and 100°C does not vary by more than 10% and, preferably, varies by less than 5%.

In accordance with a preferred embodiment of the invention, the tread underlayer also has high ratios (greater than 4) between the rigidity in the direction of travel (i.e. in the circumferential direction) and in the direction perpendicular to it; this means that it has an anisotropic behaviour.

The properties of the tread underlayer indicated above may be obtained using a compound reinforced with a quantity of fibres preferably ranging between 3 and 10 phr (parts per hundred of rubber), and even more preferably between 6 and 9 phr, in combination with hardening resins; the latter are preferably based on resorcinol and methylene donors.

These resins may be either in the form of two components or in the precondensed form, while preferred methylene donors include hexamethoxymethylenemelamine (HMMM) or hexamethylenetetramine (HMT); the Applicant has found, however, that other methylene donors and other types of hardening resins may be used.

These and further features of the invention will emerge more clearly from the detailed description of a preferred but not exclusive embodiment thereof, which is provided below with reference to the accompanying drawings, wherein:

- Fig. 1 shows a cross-sectional view of a tyre according to the invention;
- Fig. 2 shows in detail a cross-sectional view of the tread of the tyre of the preceding figure.

In the drawings, reference 1 indicates a tyre according to the invention.

This tyre comprises a carcass provided with at least one ply 3, the ends 3a thereof are associated with respective cores 4 (commonly known as bead wires), each of which is incorporated in a bead 5 defined along the inner circumferential edge of the tyre; the core or bead wire 4 of the beads may be constructed in any manner known in the art, for example using metal wires or cords.

The beads 5 are intended to rest against the edge of the rim, not shown in the drawings, on which the tyre 1 is mounted.

Around the carcass there are circumferentially applied one or more belt layers 7, made conventionally with a meshwork of metal strands or cords embedded in a rubber sheet, and arranged parallel to each other in a layer and crossed with respect to those of the adjacent layer.

Above the belt 7 there is the 0° layer in which a cord 8, for example made

of nylon, is spirally wound coaxially with the tyre; the winding angle of the cord 8 is, as usual, small with respect to a median plane m-m of the tyre and said cord is also incorporated in a rubber layer, as is commonly performed in the art (using so-called "strips" or other solutions).

The tyre 1 also has a tread band 10 which is peripherally mounted around the 0° layer; more specifically, this tread band is of the "cap and base" type formed by an underlayer 11 and an external layer 12 on which a tread pattern, comprising recesses and grooves 13 that define a plurality of seams and blocks, is formed in a conventional manner.

As can be seen in the Figures, the underlayer 11 of the tread 10 in this case has a uniform thickness; preferably this thickness is greater than 1 mm and, even, more preferably, is between 1.5 and 2 mm.

It must be pointed out, however, that the thickness of the underlayer 11 may in any case not be uniform but, for example, greater in the vicinity of its outer edges (with reference to the cross-sections shown in Figs. 1 and 2) and/or in the central zone.

The external layer 12 of the tread band must have a thickness at least equal to, and preferably greater than, that of the grooves 13 (usually 7-8 mm in car tyres), so as not to allow the underlayer to come into contact with the road when the external layer is worn.

The compound from which the underlayer 11 is formed, preferably based on natural rubber, is preferably reinforced with aramide fibres, in this case made from Kevlar® produced by the company Du Pont de Nemour; in the present example these fibres have a configuration with a main trunk having a diameter D equal to about 10 µm and a length L of about 200 µm, from which small branches or fibrils extend.

In this way the fibres have an aspect ratio L/D of the order of 20 units.

In particular, a material has been used in which the abovementioned fibres (commonly known as "Kevlar® pulp") are dispersed in a natural rubber, thereby giving rise to a "masterbatch" distributed by the company Du Pont under the

tradename Kevlartex®, having a composition of 23 % Kevlar® and 77 % natural rubber.

The use of the masterbatch instead of the fibres alone is to be preferred, because it allows to mix and apportion them more effectively with the elastomer compound which is used to produce the underlayer 11.

The composition of the compound of the underlayer is shown in detail in Table 1, where for the various elements the common tradename and a brief chemical definition are indicated.

Thus, for example the abbreviation E-SBR followed by a number is conventionally used to indicate a type of synthetic emulsion-polymerized rubber ("Styrene Butadiene Rubber"), in accordance with conventional international standards (normally ASTM or ISO), or the abbreviation consisting of the letter N followed by a number indicates the type of carbon black in the ASTM nomenclature.

The numerical values shown in Table 1 refer to the percentages with respect to the rubber (phr) and the overall compound; in the case in question it just has to be mentioned that the compound used contains 39 phr of Kevlartex® and therefore, in view of the composition of this masterbatch, it means that basically the 39 phr present are divided up into 30 phr of natural rubber (NR) and 9 phr of aramide fibres.

TABLE 1

COMPOSITIO	N OF THE UNDERLAYER COM	1POUNI	)
Ingredient	Description	phr	%
NR .	Natural rubber	30.0	14.45
E-SBR 1712	23% bond styrene, oil extended	55.0	26.49
Carbon black	Series N300	60.0	28.90
Zinc oxide	ZnO	8.00	3.85

Crystex® OT 33	67% insoluble sulphur	5.25	10.52
orysions or 55	67% insoluble sulphur	5.25	2.53
	(oiled)		
C17707@ 062	T. T		
Cyrez® 963	Hexamethoxymethylene-	5.00	2.41
(hardening resin)	melamine (HMMM)		
	65% a silica supported		
Rhenogran	80% polymer supported	1.88	0.91
Resorcinol® 80			
(hardening resin)			
DCBS	N,N'- dicyclobenzothiazole-	1.50	0.72
(accelerants)	sulphamide		
6 PPD	Para-phenylenediamine	2.00	0.96
(anti-oxidant)		·	
Kevlartex®	23 % Kevlar®, 77% NR	39.0	18.78
TOTAL		207.63	100
TOTAL		207.63	100

It is specified here that Crystex® OT 33 is distributed by the company FLEXIS, Cyrez® 963 by the company CYTEC and Rhenogran Resorcinol® 80 by RHEIN-CHEMIE.

As can be seen from the table, in this example of the invention hardening resins based on resorcinol and methylene donors (in particular HMMM) in the form of two components have been used.

The preferred methylene donors include, in addition to HMMM, hexamethylenetetramine (HMT); other donors, however, could also be used and the hardening resins may also be in the precondensed form.

As an alternative to the resins mentioned above, other hardening resins may be used, such as, for example, those based on epoxides-polyols, epoxides-diamines, epoxides-dicarboxylic acids or resins obtained by reacting alcohol with a diacid (alkyd resins).

These resins may be used either in precondensed form and in the form of

two components.

From a general point of view it can be stated that the quantity of hardening resins utilized in the compound of the underlayer, may be optimized depending on the mechanical properties (modulus, hardness, etc.) which are to be obtained.

Consequently, in the present invention, if resins based on resorcinol and methyleene donors are used, it is preferable to use a quantity of precondensed resin greater than 0.5 phr. In the case of two-component systems, however, it is preferable to have a quantity of resorcinol greater than 0.5 phr and a quantity of methylene donor (type HMMM) which is in a ratio of between 0.5 and 3 therewith.

The underlayer 11 obtained with the compound according to the invention may be coextruded together with the external layer 12, or may be formed separately and assembled together with the latter subsequently; coextrusion is, however, preferable for obtaining underlayers of limited thickness and if necessary for shaping their profile.

The compound of the above tables was subjected to a series of mechanical tests for determining the values of some of its properties, including the hardness and the elasticity; the results of these test are shown in the following Table 2.

With regard to the hardness, tests were carried out in accordance with the standard ASTM 1415 and with regard to the elasticity, the experiments consisted in measuring the dynamic modulus E' on cylindrical test-pieces with a diameter of 12 mm and height of 25 mm.

In particular, these test-pieces were formed by rolling up strips slightly wider than 25 mm (i.e. the height of the test pieces themselves), which were obtained by calendering a 1 mm thick strip cut in the direction of orientation of the fibres inside it; following rolling-up of the strips, the fibres are then arranged in the circumferential direction with respect to the cylinder which forms the test piece.

It is reminded here that the operations of calendering and extrusion of the compound produce the effect of orienting the fibres incorporated in the compound, along the respective directions with which they occur.

The test pieces were then vulcanized for a duration of 30 minutes at 151°C and subjected to dynamic tests performed with a (sinusoidal) frequency of 100 Hz, applying an initial pre-strain of 10 % and a true dynamic strain equal to 0.033; this latter variable represents the deformation in relation to the length of the pre-deformed test piece.

Further variables taken into consideration during the tests, the results thereof are shown in Table 2, include the load at 10 % of elongation strain in the calendering direction (M1) and in the direction transverse thereto (M2).

Such load values were obtained in accordance with the standard ASTM 412, by subjecting to traction traditional test pieces of the Dunbbell type; they provide an evaluation of the strength of the underlayer in mutually perpendicular directions. The ratio M1/M2 shown in the table constitutes an index of the anisotropy of the underlayer due to the presence of the oriented fibres.

Finally, in order to appreciate more fully the features of this example of the invention, Table 2 also shows the results of comparative experiments carried out on samples of compounds corresponding to the already mentioned European patent EP 592218 (Sumitomo Rubber Industries) and patent CA 1228282 (Bridgestone), respectively.

TABLE 2

TESTS	Invention	Example 2	Example 3
IRHD at 23°C	90	89	77.5
IRHD at 100 °C	89	83	67.4
Load M1 at 10 % elongation in the calendering direct-ion (MPa)	11.77	11.62	2.5
Load M2 at 10 % elongation in the direction transverse to that of calendering (MPa)	1.23	1.5	2.05
M1/M2	9.6	7.75	1.22

E' 23°C (MPa)	36.71	34.91	11.42
E' 70°C (MPa)	33.18	20.32	7.16
E' 100°C (MPa)	33.15	16.67	5.7

From Table 2 it can be appreciated how the compound according to the invention is much more stable with respect to the temperature (thermostable), than those of Examples 2 and 3.

In particular the hardness is very stable between 23°C and 100°C (ranging from 90 IRHD to 89 IRHD within the limits of the measuring range); more generally, the hardness variation must in any case not be greater than 5 IRHD in the abovementioned temperature range.

In accordance with the invention the hardness of the underlayer, in terms of absolute value, is preferably greater than that of the external layer of the tread band; more specifically, this hardness must be preferably greater than 80 IRHD at 100°C and, even more preferably, greater than 85 IRHD at 100°C.

Likewise the hardness, also the elastic modulus E' in the case of the invention is not subject to major variations between 70°C and 100°C, whereas the same cannot be said for the compounds of Examples 2 and 3.

Preferably the variation of the elastic modulus E' is not greater than 10 % and, even more preferably 5%, in the abovementioned temperature range.

In accordance with the invention, the absolute value of the elastic modulus E' of the underlayer is preferably greater than that of external layer of the tread band: more specifically, this modulus must be preferably greater than 15 MPa at 100 °C and, even more preferably, greater than 20 MPa at this temperature.

The Applicant has realized that, with the values for hardness and/or elastic modulus E' mentioned above, a substantial qualitative increase in all the known tyres is obtained, independently of the characteristics of the external layer of the tread band.

Finally, from Table 2 it may be noted how the ratio M1/M2 for the example of the invention is greater than 9; more generally, this ratio must be

greater than 3.

For the sake of greater completeness of the description, there are now reported the compositions of the underlayer compounds relating to Examples 2 and 3, obtained on the basis of the descriptions of the patents mentioned above.

TABLE 3

	EXAMPLE 2	EXAMPLE 3
Ingredient	(phr)	(phr)
NR	26	
E-SBR 1712		137:5
SBR 1500	20	
Carbon black (N324)	40	
Carbon black (N326)		90
Zinc oxide	3	3
Sulphur	1.75	1
Accelerants	1	1.8
Anti-oxidants	2	2
Kevlartex®	74	
	1	

From the point of view of performance, the tyres manufactured in accordance with the invention have achieved surprisingly superior results compared to other tyres of the HP and UHP type; these results are summarised in the following Table 4 showing ratings on a scale of values ranging from -2 a + 2, in respect of particular behavioural parameters of the tyres.

These parameters relate to the behaviour during bends (oversteering and understeering), grip, lateral stability, response to lane changing and performance constancy; this latter index refers to the ability of the tyre to keep unchanged the level of performance at high speeds and consequently with an increase in temperature.

The tests were carried out using tyres of size 255/40 R 17, mounted on the rear axle of a Porsche Carrera 996.

TABLE 4

	INVENTION	EXAMPLE 3
Steering	2	1.2
Grip	2 .	2
Lateral stability	2	1.5
Lane changing	2	1
Performance	2	1.3
constancy		

As can be seen, Table 4 confirms what was stated above regarding the results achieved by the invention; the tyre, indeed, achieves excellent results for all the parameters considered, obtaining the maximum rating in all the categories and being remarkably superior to the tyre of Example 3, with the sole exception of the grip.

Indeed, it must be emphasized that such an exception further confirms the results obtained.

In fact, as is known, the grip of a tyre depends in particular on the compound of the "cap" of the tread and not on that of the underlayer; in this case, since the same compound has been used for the external layer of the tyre according to the invention and that of the tyre according to Example 3, the data relating to the grip is itself consistent with that which could be expected.

This confirms therefore how the better performance achieved by the tyres according to the invention for the other parameters considered, are to be attributed to the underlayer 11 and to the compound from which it is made.

Finally it is important to point out also another advantageous aspect which distinguishes the compound from which the underlayer according to the invention is made: its good processability.

During experiments it was found that an excessive quantity of fibres with respect to the rubber of the compound (i.e. exceeding the ranges suggested by the invention), may negatively influence the processability of the said compound and cause problems for the subsequent production of the tread with the underlayer.

The quantities of reinforcing fibres used for the invention have, on the other hand, managed to eliminate these negative consequences, thereby making the invention very advantageous from the point of view of industrial production.

Obviously variations of the invention may be envisaged with respect to the preferred and non-exclusive embodiment thereof which was described above.

At first it must be pointed out that the reinforcing fibres used may be different from the Kevlar® mentioned above; other aramide fibres may indeed be used, such as for example those known with the name Twaron® and distributed by the company Akzo Nobel; also in general the Applicant has found that it is possible to use fibres based on other polyamides or on polyesters, polyolefins, polyvinyl alcohol, nylon, glass or the like.

As regards the structure of the tyre, the usual thin joining sheet may be inserted between the 0° reinforcing layer and the tread underlayer, as already occurs in the known art.

These changes, together with others, fall however within the scope of the claims which follow.